Concepts of Chemistry for Engineering
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Lecture – 36
Magnetism

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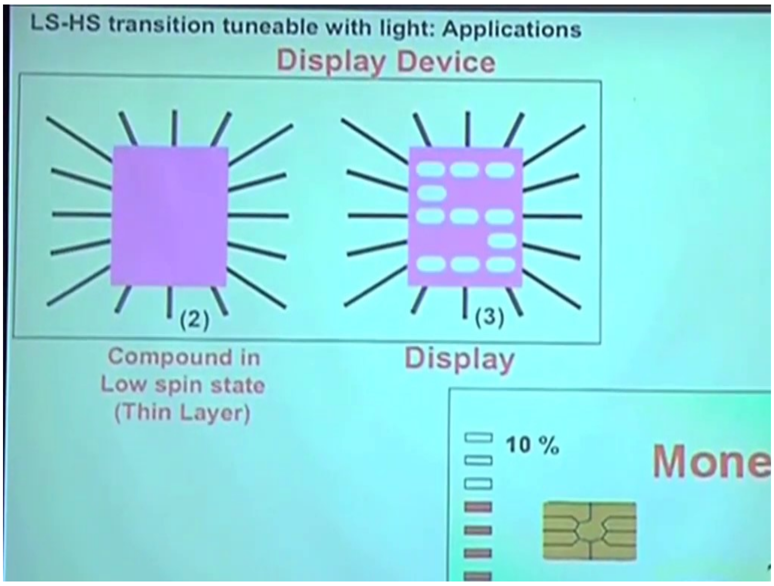

LS-HS transition tuneable with light: Applications

Display Device

Compound in Low spin state (Thin Layer)

Display

Alright, I will start on magnetism, before going to magnetism I think one or two application what we were discussing for coordination chemistry I will show in here. Sometimes we do not realise that the simple high spin, low spin configuration can give you something very, very important.

For example, let us say you have a complex which is low spin, it has one colour, low spin, you know what sort of transition you do expect, it can vary depending on the compound. Let us say you have a given compound, the compound is low spin, if you give the temperature, if you heat the complex, what you can have is, you can convert the low spin compound into high spin because low spin means what, those spin cannot go in the eg orbital let us say, t2g2 eg orbital.

Now, as soon as you put heat or, let us say laser light, some of the spin, some of those electron will be now travelling to the eg orbital, t2g2 eg. Now the colour of that compound will be different. It could be white to red, red to white, or whatever it is. So, by changing these something like display you see, lot of these colour display, in big audience or big auditorium or even display in the, on roadside somewhere else.

So basically, let us say it is one colour, the moment laser light is signing on this display, what happens, it may be showing a particular thing, particular let us say name written whatever you want to happy birthday wish that something you have wished me that can be written over here on the board just by signing those laser lights, that is nothing but changing high spin to low spin configuration, lot of things can be done and it has been done without realising we are seeing those.

Other form of these sort of high spin low spin conferring configuration can be used in your money card or ATM. Let us say you have a debit card, you have 10,000 rupees every time you pick up money, let us say first time you pick up 2000 rupees from ATM machine. Now, so, what can happen is a selected amount of laser light can be irradiated on your card, because 2000 rupees will, let us be selecting by default how much laser light to sign, thereby some of the complex will go from high spin to low spin or low spin to high spin, let us say low spin to high spin.

Specifically, you are putting light so low spin to high spin will be going. Next time when you are punching the card again, the machine can read how much money you have left, let us say after 10,000 minus 2000, 8000. This way, let us say at the end you have 1000 rupees you want to draw 5000 rupees from that, instrument will not allow.

So, these are also technique, these are different ways to take advantage of this complex, this is something one paper has already come. And only problem is so far this technique is a little bit expensive. That is why we do not see it in the market right now. But soon enough, it will be made, hopefully made cheaper, then you can the technology itself is coming expensive. That is why it is not in the market. But in principle it can be done.

So, lot of the practical application just by signing light, since just by signing light, you can change the electronic configuration of a compound. Of course, you have to choose the right compound, right wavelength, right everything let us say, but once you have that right combination you can do wonder, something like this.

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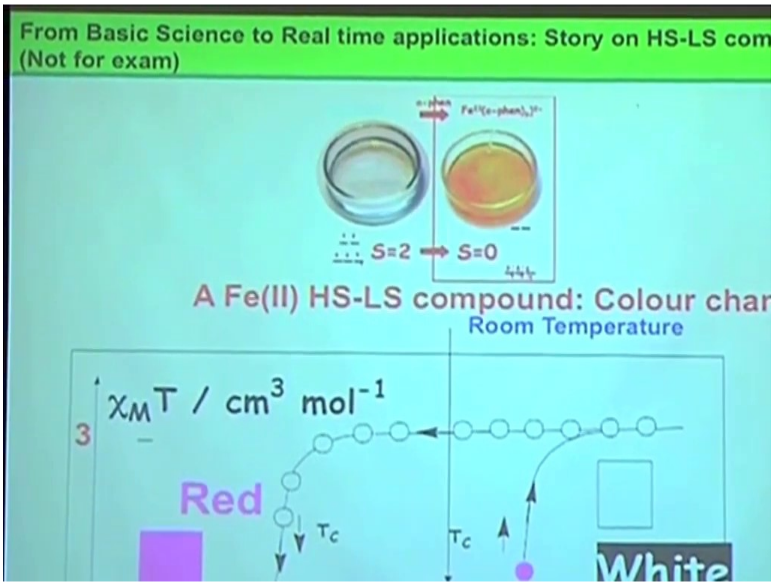

From Basic Science to Real time applications: Story on HS-LS com
(Not for exam)

A Fe(II) HS-LS compound: Colour char

Also, other things of course, you know that you have a colourless compound, you add something high spin to let us say low spin complex form or low spin to high spin complex form something like you cannot read here this is a iron aqua complex which is colour less you, the moment you add phenanthroline to it, high spin complex becomes low spin complex, colour changes.

Another so this is of course some time you can use it for magic, lot of other application you can have simple colour change. Other things for example, if you have let us say this red complex, red complex is due to the low spin complex, red complex is due to the low-spin complex.

For example, you starting with that, the you are heating it. So, this is the temperature initially it was 250 Kelvin that is almost like room temperature let us say, you start from there you keep on heating, nothing happening, nothing happening, select at a selected temperature now the low spin to high spin transition is going on, then what you will see, all of a sudden at a particular temperature this red compound is becoming white.

So, at that let us say this is 325, this is becoming white. Now that white compound you can try to pull down, it will not follow exactly same pathway because the relaxation of the spin like spin was up, spin has to go down that relaxation need not be necessarily following the same path, you have excited something, the relaxation means coming back from the eg level t2g level need not follow the same temperature profile, what it can happen is, at after reaching this white colour, it will take quite some time to come back to the red colour.

So, that even if you are decreasing the temperature still it stays white and at a particular temperature cooling down at a particular temperature can bring you red. So, these are nothing, this is like a very good some these sort of behaviour you can apply to something which, which may be let us say I mean it could be let us say what I said for money card your ATM card, it could be for other display device, lot of other things you can, you can do.

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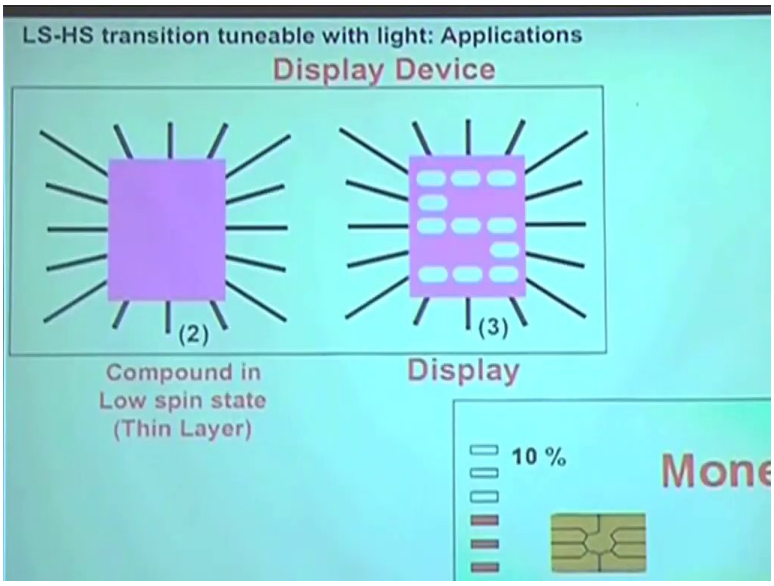

LS-HS transition tuneable with light: Applications

Display Device

So, display device for example, it is here you just sign the light so, it is getting heated thereby some red colour or let us say purple colour it is coming white colour even if you pull down significantly, this white colour may not go back to red very quickly. But then again there are different material which can relax faster that means high spin to low spin it can come down faster.

So, you sign the light, the whatever we say whatever lightening is there you see it, you take off the light, it goes back to the white or red or blue or sorry, this purple again. So, you can, you can basically dictate the term, you can tell what you want, thereby which complex to pick, you want to sign the light from, let us say violet colour or red colour, you want to go to white colour and you want to stay in white that is one of the mode or if you want to go back right after switching of the laser that can be also possible.

So, these are nothing but application in different display which you can have based on the synthetic chemistry knowledge. Of course, lot of start-up companies and a lot of other related application in material science has already come up. These are something of course you can in future, if you are looking for a start-up companies. Something that these knowledge is necessary, is not necessarily this knowledge, it is some other knowledge you read in let us say fourth year, fifth year, or sorry fourth year. So, you can, you can take it off and try to set up a company from the simple ideas if there is non-existing.

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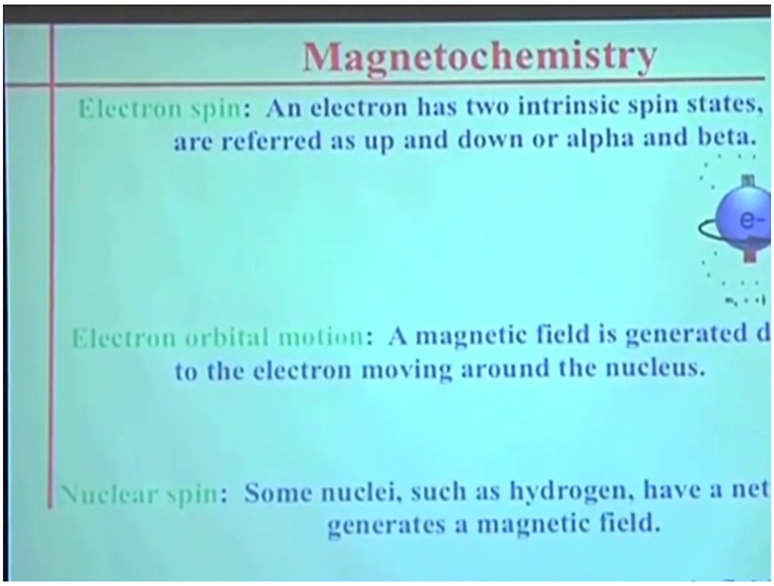

Magnetochemistry

Electron spin: An electron has two intrinsic spin states, are referred as up and down or alpha and beta.

Electron orbital motion: A magnetic field is generated d to the electron moving around the nucleus.

Nuclear spin: Some nuclei, such as hydrogen, have a net generates a magnetic field.

So that is I guess that knowledge sharing and today we will discuss mainly magnets. We were discussing magnets in the last class, simply magnets are nothing but having or magnetic compounds are nothing but having unpaired electrons, that is what we are discussing, more than unpaired electron better the magnetic moment or higher the magnetic moment, magnetic values will be high.

If you have paired up all the spin paired up, if you have unpaired electron, but those unpaired electrons are not unpaired, they are pairing it up, then you are losing the magnetic values, magnetic moment value. So, all the complexes can potentially therefore give you magnetic moment, because all of them are having electrons.

Now that electron as we were saying, electrons are rotating around its own axis. That is the spin value. It is spinning, that is why it can give you one type of momentum or spin or spin angular momentum or sorry, it is called spin only values for magnetic moment or it can rotate around the orbital. There is a nucleus surrounding it, the electrons are rotating.

So, these are the two types of motion that can give you magnetic moment. But what we are saying usually, you do not have to worry about the orbital component, only the spin only value good enough, because ligands are restricting the electrons, because they are overlapping effectively, restricting the electrons to rotate around the orbital.

So therefore, since the electrons cannot really valence electron mind you, not the inner electron, valence electron not effectively able to rotate around its own orbit or rotate along its orbit, you end up getting only spin component, only spin magnetic moment value you get.

Now, also, we were trying to tell you that some cases you have to have spin value plus some orbital contribution. Why is that? That is simply because those whenever one orbital to another orbital transition is possible, I guess last class we were trying to discuss. So let us say dxy to dyz to dxz, these transitions are allowed transition, because by rotating just 90 degree, you can interconvert these orbital.

Therefore, you can see there is a magnetic component, let us say from xy direction to a xz direction. So thereby there is a some, some sort of magnetic contribution on the z direction. It is, it is not necessarily ligand is holding the electron completely, it is retarding it, it is preventing it but not 100 percent.

The moment electron can transfer from one orbital to another orbital that means that direction changes xy direction to xz direction, z direction some component will be arising that is the one going to give you the orbital contribution. I will come back to that again. Let me tell you again simply electron can spin therefore, magnetic moment values can come out of it, but opposite spin can cancel each other as we were trying to say.

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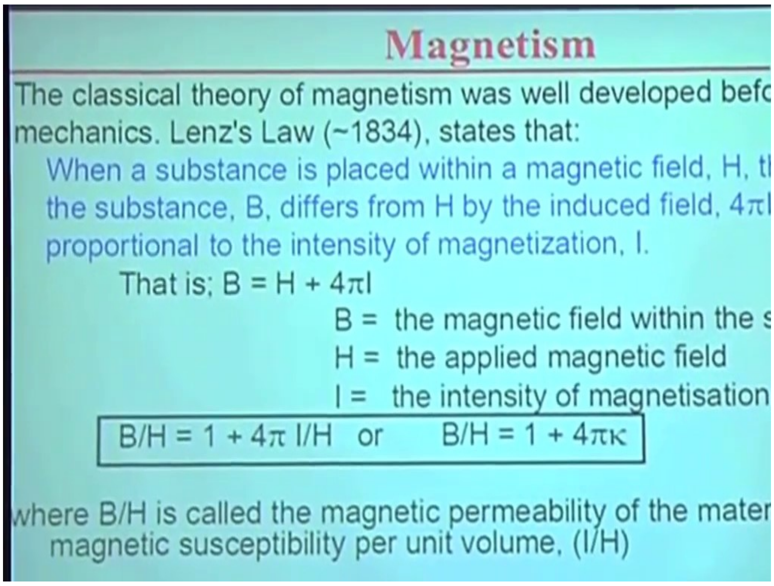


Magnetism

The classical theory of magnetism was well developed bef
mechanics. Lenz's Law (~1834), states that:

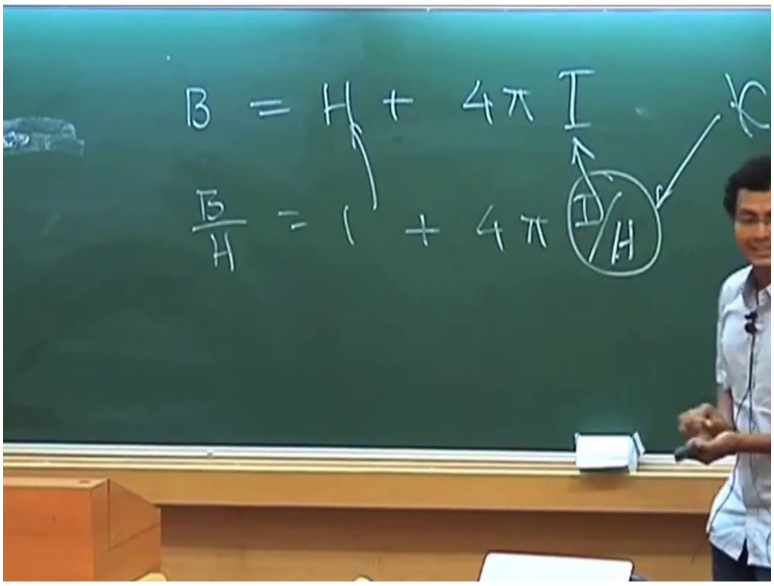
When a substance is placed within a magnetic field, H, t
the substance, B, differs from H by the induced field, 4πI
proportional to the intensity of magnetization, I.

That is; $B = H + 4\pi I$

B = the magnetic field within the s
H = the applied magnetic field
I = the intensity of magnetisation

$$\boxed{B/H = 1 + 4\pi\, I/H \quad \text{or} \quad B/H = 1 + 4\pi\kappa}$$

where B/H is called the magnetic permeability of the mater
magnetic susceptibility per unit volume, (I/H)



Overall, I guess overall, we in terms of mathematical calculation, we can have this equation where, where essentially you are keeping your molecules in a magnetic field and that that magnetic field is going to be your H so, in let us say, this is the magnetic field of H. Here you are keeping the compound, so, how much magnetization or how much effect this molecule is going to feel that is dependent on the magnetic field that H, plus its characteristics, its its nature, what can it be magnetised pretty easily? That is the term called I, so any species kept in a magnetic field is going to feel the field itself plus its inherent behaviour that will try to make it magnetised. So, that is the I component.

Now, so, intensity of magnetization, how quickly it can, it can or how greatly it can orient with respect to that magnetic field. Now, if you do the math so, B by H if you divided, divided by H, B by H will be 4 pi I, I by H, this term is called this kappa or the magnetic susceptibility. So, this is the term kappa is the magnetic susceptibility.

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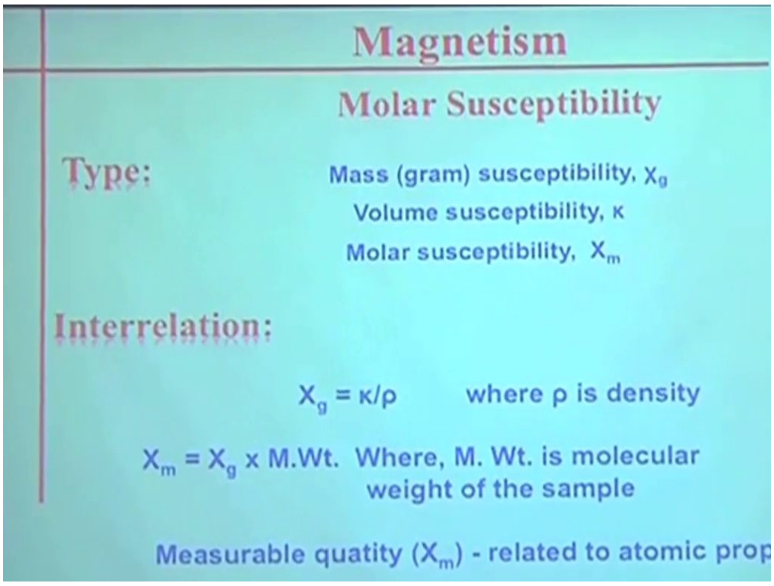

Magnetism

Molar Susceptibility

Type:

Mass (gram) susceptibility, χ_g

Volume susceptibility, κ

Molar susceptibility, X_m

Interrelation:

$X_g = \kappa/\rho$ where ρ is density

$X_m = X_g \times$ M.Wt. Where, M. Wt. is molecular weight of the sample

Measurable quatity (X_m) - related to atomic prop

Now, from there you can do the following math simply there is Kappa by rho which is the density of the species, density of the molecule that will be the gram molar, grams magnetic susceptibility multiply that with molecular weight that will be molar, molar susceptibility so this I by H term, you divided by rho simple its density of the molecule you get kai G or x this magnetic susceptibility gram magnetic susceptibility.

This term you multiply by molecular weight you get molecular or sorry, this molar susceptibility, this is just simple math. You have this equation divide by H you get I by H which is Kappa, divide Kappa by rho that is going to be your gram susceptibility or mass susceptibility. Mass susceptibility multiplied by molecular weight you are going to get the molar susceptibility; it is something I think you have studied before.

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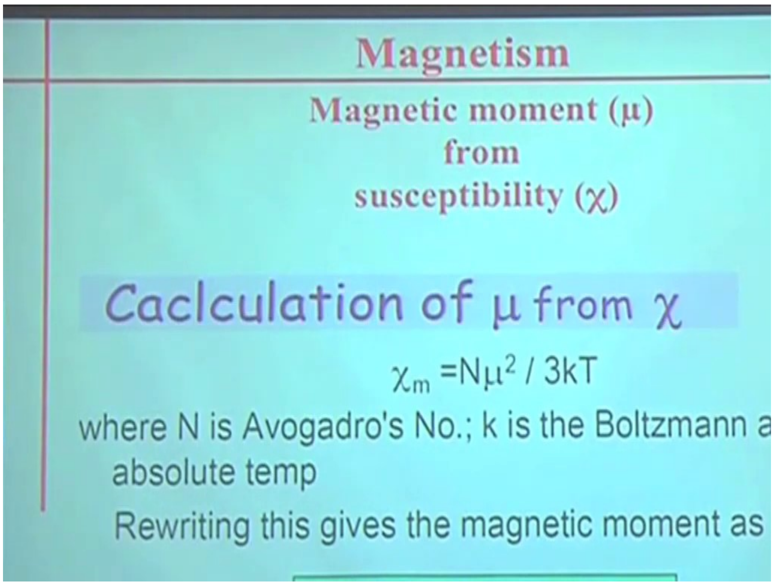


Magnetism

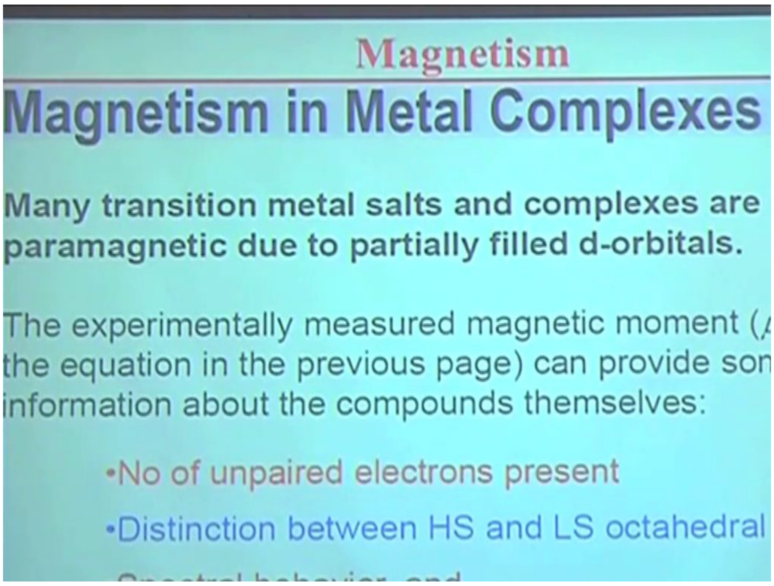
Magnetic moment (μ)
from
susceptibility (χ)

Caclculation of μ from χ

$$\chi_m = N\mu^2 / 3kT$$

where N is Avogadro's No.; k is the Boltzmann a
absolute temp

Rewriting this gives the magnetic moment as



Magnetism

Magnetism in Metal Complexes

Many transition metal salts and complexes are paramagnetic due to partially filled d-orbitals.

The experimentally measured magnetic moment (
the equation in the previous page) can provide so
information about the compounds themselves:

- No of unpaired electrons present
- Distinction between HS and LS octahedral

Now, once you have that molar susceptibility that is corresponded with the magnetic moment, this is the simple equation. Now, from there, you can get the magnetic moment value of a compound. Of course, mu you can calculate what it is coming it has a temperature component. So, what it tells you is the temperature is going to affect your magnetic moment value, we are going to see how it is affecting.

The magnetic moment value is the one we were talking it has two component. The spin component and the orbital component. Now, this magnetic moment value can give you the idea about the complex itself, what it is made of, how many unpaired electron it has, this is a experimentally measurable quantity, you can measure the magnetic moment value and thereby you can get crucial information about your let us say unknown compound.

It can give you number of unpaired electrons present, high spin, low spin, it can give you the spectral behaviour, it can, it can also tell you something about the structure of the complex. So, what all we are saying is if you have an unknown complex, you can measure the magnetic moment value of it and thereby you can try to tell what that compound is made of, how the equation, equations are we have seen in here.

These are two different equation, one is this one, another is this one as long as you know the relationship between these two equation, you are good to go. This is simple connection between them you just figure it out between these two equation, this equation and that equation. They are connected by this Kappa I by H and then Kappa divided by your density will give you molar susceptibility and then multiplied by my molecular weight, you just look two minutes it should be clear.

So, based on these equations and it is expected usually one of the math is given. Usually, we get one question at least based on these two equations, their interrelation, some value will be given and thereby you have to calculate the magnetic moment let us say, usually also in the I think maybe it is in the tutorial question as well, I forgot.

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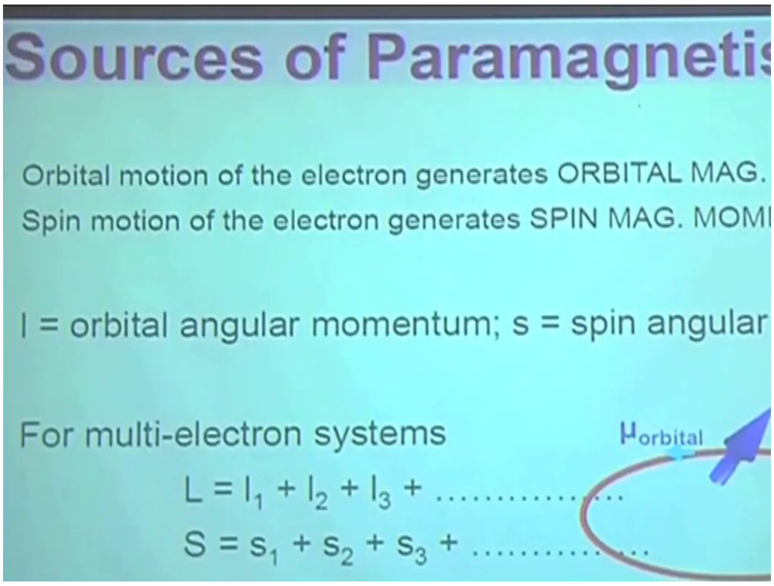

Sources of Paramagneti

Orbital motion of the electron generates ORBITAL MAG.
Spin motion of the electron generates SPIN MAG. MOM

l = orbital angular momentum; s = spin angular

For multi-electron systems

$L = l_1 + l_2 + l_3 + \ldots\ldots\ldots\ldots\ldots$

$S = s_1 + s_2 + s_3 + \ldots\ldots\ldots\ldots\ldots$

Now, we, we were talking in the last class as well and today itself also we have two components, orbital component and spin component. The resultant one is going to be the mu total, but these orbital component is going to be nullified or it will be diminished, decreased not necessarily you can prevent it 100 percent, that is the orbital contribution. Usually, we do not have to worry about orbital contribution, you can calculate just mu spin only. The equation for calculating this mu total by taking this orbital and spin contribution is this one.

Now, what happens to that capital S, this S is number of unpaired electrons in their spin, if it is three unpaired electron half plus half plus half, 3 by 2. L, L will that will come, come will come for the lanthanide section, it is the summation of usually ML. So, for d orbital it is let us say plus 2, plus 1, 0, minus 1, minus 2, will come for the lanthanide from there we will discuss. Anyway, you do not have to calculate for d block element, you usually do not have to calculate the L values, you can only plug this equation for the S value.

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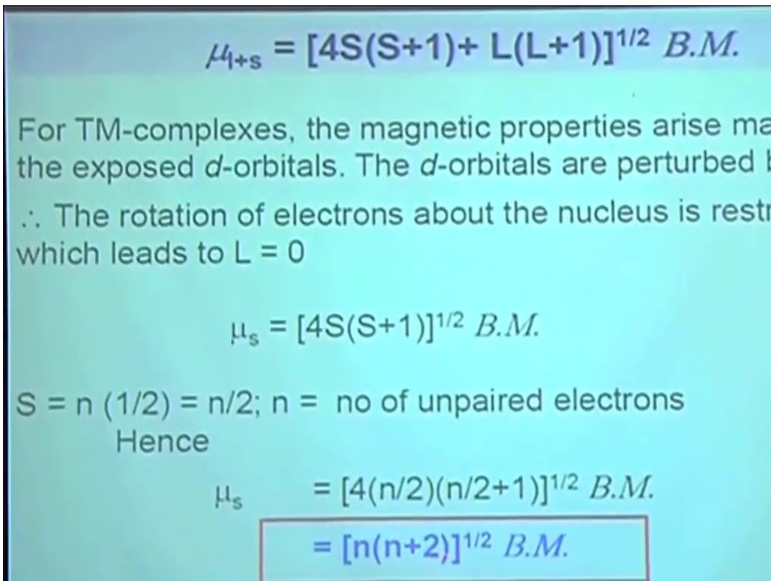

$$\mu_{l+s} = [4S(S+1) + L(L+1)]^{1/2}\ B.M.$$

For TM-complexes, the magnetic properties arise ma
the exposed *d*-orbitals. The *d*-orbitals are perturbed
∴ The rotation of electrons about the nucleus is restr
which leads to L = 0

$$\mu_s = [4S(S+1)]^{1/2}\ B.M.$$

S = n (1/2) = n/2; n = no of unpaired electrons
Hence

$$\mu_s = [4(n/2)(n/2+1)]^{1/2}\ B.M.$$

$$\boxed{= [n(n+2)]^{1/2}\ B.M.}$$

So, we have two component once again only spin value is good enough. What you nail it down further is root of n multiplied by n plus 2, in n times n plus 2 root of that, that gives you for one unpaired electron, two unpaired electrons, three unpaired electrons, four and five and so on, what would be the magnetic moment value?

So, by knowing how many unpaired electron is there pretty much you can be confident what will be the experimental or experimentally observed magnetic moment for pretty much a lot of cases. Now so that is the magnetic moment value, but often what you see is at the end of it the experimentally observed magnetic moment value is slightly higher sometimes a lot higher. How those are coming from, or where they are coming from, that is due to the assumption that this component does not exist, we bring them back to explain it.

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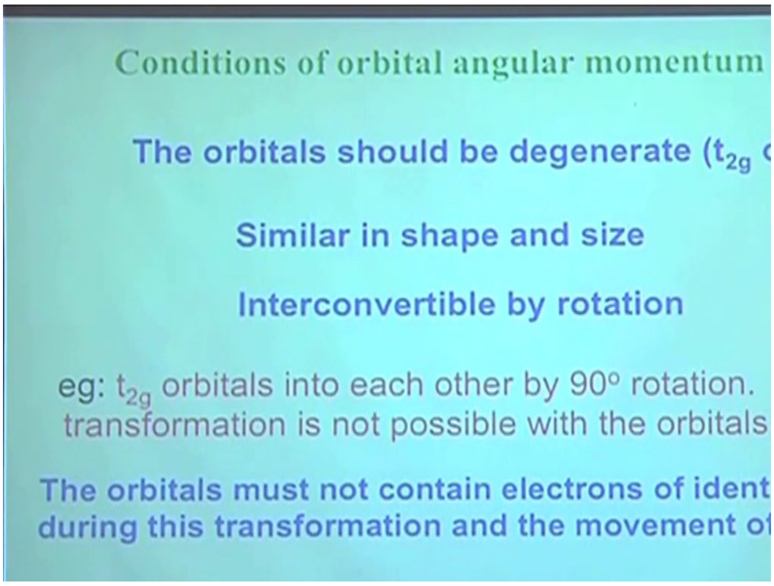

Conditions of orbital angular momentum

The orbitals should be degenerate (t_{2g}

Similar in shape and size

Interconvertible by rotation

eg: t_{2g} orbitals into each other by 90° rotation.
transformation is not possible with the orbitals

The orbitals must not contain electrons of ident
during this transformation and the movement o

So, when you need to when the orbital angular momentum that mu L part comes in, it comes in when you have degenerate orbital, we have degenerate orbital, if d orbital was not splitted then this component would have been high, if five d orbitals were degenerate, then interconversion would have been possible much easier or five of the, five of the orbital it can interconvert. So, electron can interconvert between 1, 2, 3, 4, 5.

So, therefore, the orbital so, sorry, the orbital angular momentum value would have been higher since in octahedral field for example, or tetrahedral field, it is splitted into t2g eg or et2, we are going to get a little less orbital angular momentum value, compared to unsplitted d orbital.

Now, of course, interconversion leads to some sort of new directionality xy to xz, z is new, xz to yz, y is new. So, that is the one contributing for your little bit more momentum. Now, just degeneracy is not good enough, why? Because you should be able to interconvert also. For example, dx2 y2, this is the last warning. It is a big class, if it was a small class, I would not have mind too much because I know what exactly goes on. Please have some respect.

So, what we are trying to have is t2g eg eg dx2 y2 and dz2 by no way you can interconvert. Therefore, in eg, you from eg you cannot get any orbital angular momentum value, only possibility is t2g, because dxy, dyz, dxz are interconvertible. Of course, if they are having same spin, you cannot interconvert.

So, let us say t2g3 1, 1, 1 all three of them are having same spin, you cannot interconvert, fair enough. So, inter, they are, they should be similar shape and size, dxy dyz dxz are the same shape and size, there should, they should be interconvertible and the orbital must not contain electrons of identical spin, that is the criteria for getting some orbital angular momentum, is it clear?

So t2g1 you can get orbital angular momentum because t2g1, that one unpaired electron can be either in dxy, dyz or dxz. Three different orientations are possible t2g2 is possible t2g3 is not possible, t2g4 once again is possible, t2g5 is possible, t2g6 is not possible. t2g3 all three are having same spin, from where to where you will interconvert.

See t2g1 means dxy to dyz you can go, interconvert means one, one means they have to exchange, if there is no scope for exchanging, how will you exchange. Same spin t2g3 means three unpaired spin in the same direction, spin multiplicity, same reaction they will be having you so only so far as you see only t2g3 will not be able to give you, yeah.

Student: (())(24:58)

Lecturer: That, that I am coming, yeah, next slide. So that interconversion will be having some contribution not as great as let us say t2g to t2g configuration. So, t2g2 t2g (confi) I mean interchange will give you a little bit more orbital angular momentum value, compared to eg to t2g conversion. That is, that is what the next slide is about.

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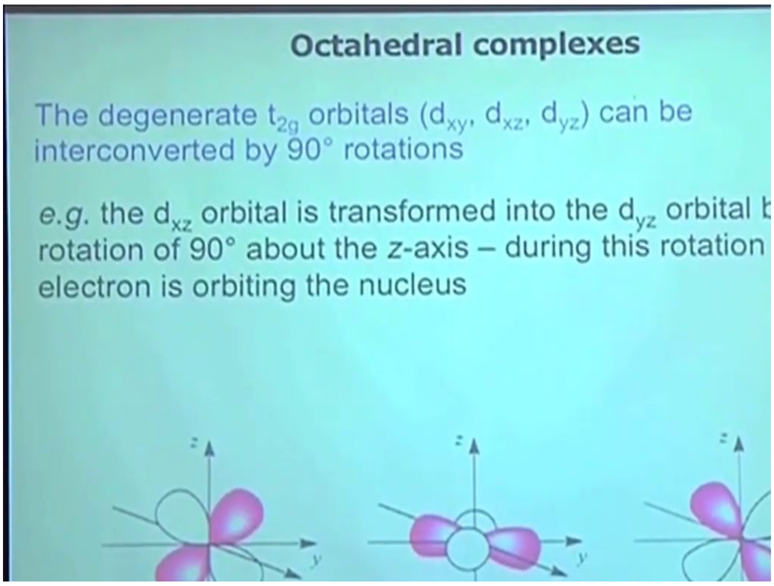
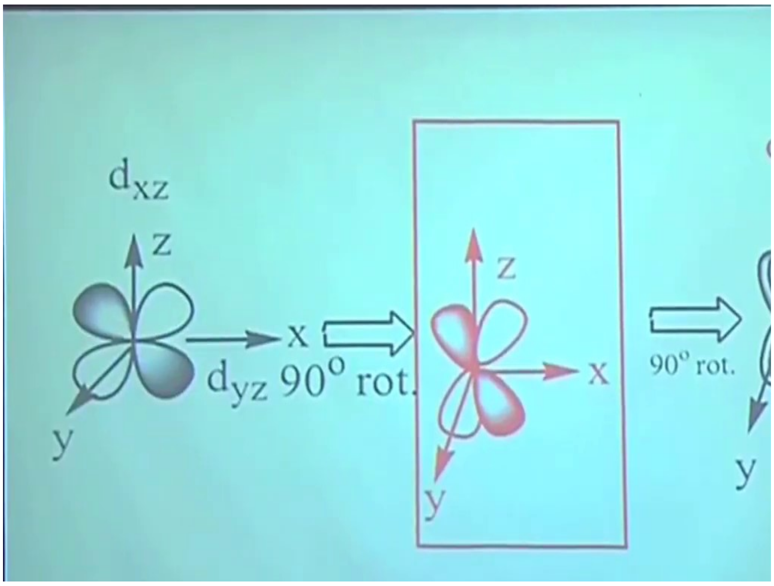
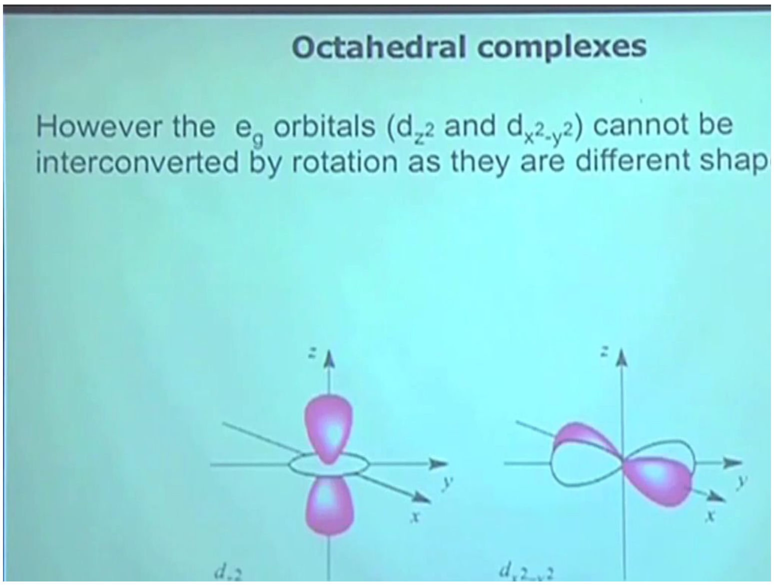


Octahedral complexes

The degenerate t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) can be interconverted by 90° rotations

e.g. the d_{xz} orbital is transformed into the d_{yz} orbital
rotation of 90° about the *z*-axis – during this rotation
electron is orbiting the nucleus




Octahedral complexes

However the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation as they are different shap

So, dyz, dxy and dxz these three orbitals are interconvertible, no problem. Over here, that is the interconversion is shown. So, you just so, you just rotate by 90 degree you will be able to rotate dxy. So, this plane to that plane to that or whatever these three different plane you can say. Now, as you see dz2 and dx2 y2 are not interconvertible so from purely from eg orbital, just eg orbital itself cannot give you any orbital angular momentum value, so the spin only value is only considered.

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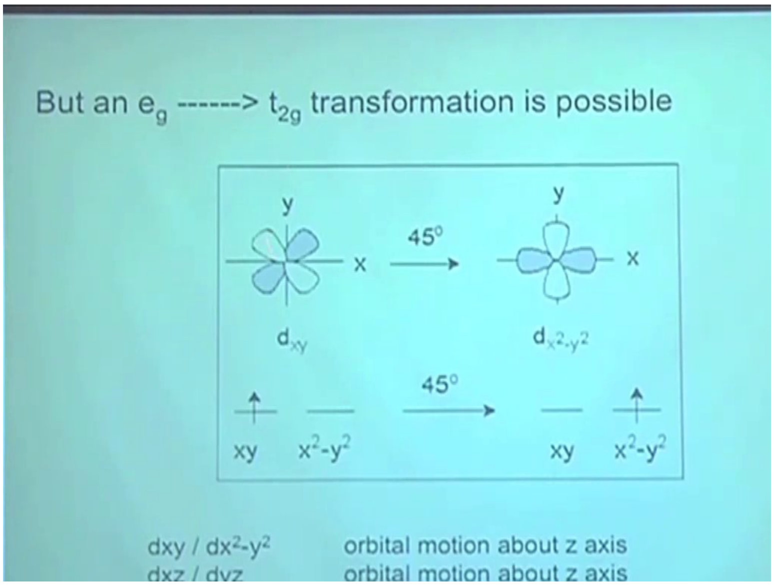

But an e_g ------> t_{2g} transformation is possible

dxy / dx^2-y^2 orbital motion about z axis

dxz / dyz orbital motion about z axis

Now, of course, for what your friend trying to say is dxy is convert, can be converted to dx2 y2, yes. And thereby, once you can convert dx2 y2 into dxy, then you can interconvert dxy dxz dyz and so on. So, t2g eg mixing, if you can have, then you will be able to get better orbital angular momentum value, but usually for mixing those energy has to be close enough if the gap is very high that mixing is not going to be possible.

So, we all hopefully by now understand that it is angular momentum or this orbital angular momentum and spin momentum value are important usually spin only value is good enough. But, in some cases, you have to talk about orbital angular momentum. Actually, that makes it little bit important or interesting otherwise, whatever unpaired electron is there, you will just end up calculating based on your calculator, that is not fun. Of course, the exam questions are asked at least one, two or so on orbital angular momentum, when orbital angular momentum is there.

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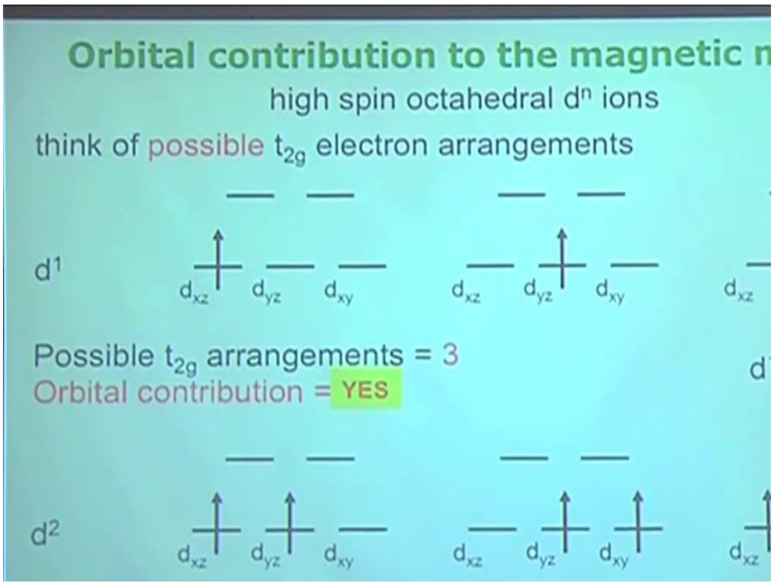

Orbital contribution to the magnetic

high spin octahedral d^n ions

think of possible t_{2g} electron arrangements

Possible t_{2g} arrangements = 3

Orbital contribution = YES

Now, so this is the same thing what I was trying to say d1 can have these three different contribution for example, titanium 3 plus is having d1 electronic configuration. And therefore, orbital contribution will be there. For example, d2 vanadium 7 plus so, how the question would be let us say, a complex is given where vanadium is sorry, where vanadium 3 plus, vanadium 3 plus and you are asked whether it will have any orbital angular momentum or not.

Or in some other form it will be asked indirectly but mostly definitely I can assure you at least one question will be there on orbital angular momentum at least if not two. So, there you can have two different or three different configuration orbital contribution possible, yes.

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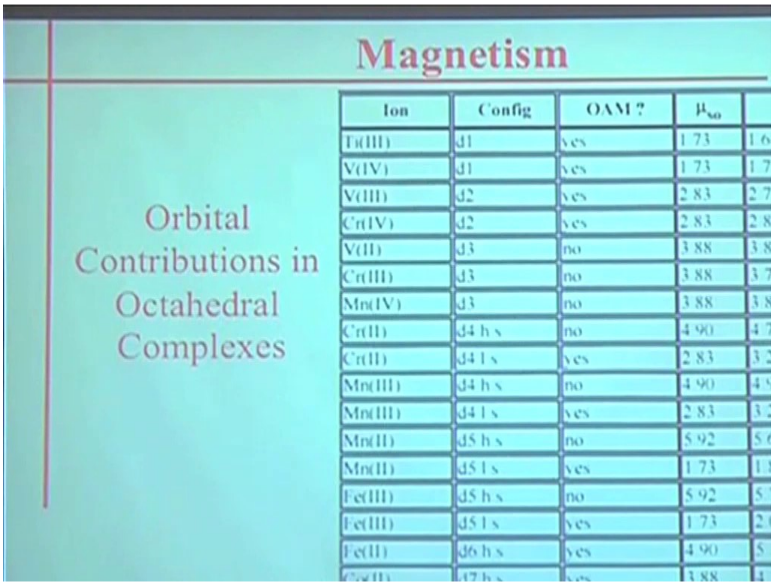

Magnetism

Orbital Contributions in Octahedral Complexes

Ion	Config	OAM ?	μ_{so}	
Ti(III)	d1	yes	1.73	1.6
V(IV)	d1	yes	1.73	1.7
V(III)	d2	yes	2.83	2.7
Cr(IV)	d2	yes	2.83	2.8
V(II)	d3	no	3.88	3.8
Cr(III)	d3	no	3.88	3.7
Mn(IV)	d3	no	3.88	3.8
Cr(II)	d4 h.s	no	4.90	4.7
Cr(II)	d4 l.s	yes	2.83	3.2
Mn(III)	d4 h.s	no	4.90	4.
Mn(III)	d4 l.s	yes	2.83	3.2
Mn(II)	d5 h.s	no	5.92	5.6
Mn(II)	d5 l.s	yes	1.73	1.
Fe(III)	d5 h.s	no	5.92	5.
Fe(III)	d5 l.s	yes	1.73	2.
Fe(II)	d6 h.s	yes	4.90	5
Co(II)	d7 h.s	yes	3.88	4.

Now, this is something you do not have to remember, but you can justify, you can go through each of those one by one. So, d1 orbital angular momentum possible? Yes, you can perhaps not read from here, that is okay. So, what we have tried to do here is given you the complex, different complex, and their electronic configuration d1, d2, d3, d4 up to d10 and then you have to write down t2g eg electronic configuration.